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De kristalstrukturen van de pentamere cyclofosfazenen N5P5Br10 en N5P5F10.

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S U M M A R Y

In this thesis the determination of the crystal structures of the cyclophosphazenes $N_5P_5Br_{10}$ and $N_5P_5F_{10}$ is described. The crystal structures of the other compounds of the group $N_nP_nX_{2n}$ with n = 3,4 or 5 and X = F,Cl or Br can be found in the literature. Thus a comparison of the crystal and molecular structures of all halogenocyclophosphazenes with n 3 to 5 is now possible. Some aspects of such a comparison are dealt with in this thesis.

In Chapter 1 a survey is given of concepts and ideas generally used in the qualitative description of molecular structure and chemical bonding of compounds of second-row elements. It is assumed that chemical bonding in the cyclophosphazenes can be separated into σ and π bonding and that 3d orbitals of the phosphorus atoms participate in the π bonding. In addition to this we have assumed that only two of the 3d orbitals contribute appreciably to the π bonding ($3d_{xz}$ and $3d_{x^2-y^2}$; K.A.R.Mitchell, J.Chem.Soc.A, 1968,2683). In planar rings, then, the total system of π bonds may be separated into an antisymmetric and heteromorphic π_a system and a symmetric and homomorphic π_s system; in non-planar rings this classification only holds approximately.

Using this theoretical model, the influence of the electronegativity of substituents, the effect of π bonding and the effect of ring size on the P-N bond lengths and the N-P-N and X-P-X bond angles are discussed.

In Chapter 2 the structure determination of $N_5P_5Br_{10}$ is described. The compound crystallizes in the space group $P\bar{1}$. The intensities of independent reflexions up to $\Theta = 30^{o}$ were measured at 110 K on a three-circle

diffractometer with Mo radiation. The structure was solved by the symbolic addition method and refined by block-diagonal least-squares analysis to R = 12.0% and R_w = 7.9% for 3260 observed reflexions. The ten-membered phosphorus nitrogen ring is puckered with one of the phosphorus atoms deviating 0.54 Å from the average ring plane and with a re-entrant angle at the opposing nitrogen atom. The molecule has a pseudo-mirror plane passing through these atoms and perpendicular to the best plane through the ring. The mean P-N and P-Br bond lengths are 1.571(17) and 2.175(6) Å. The N-P-N angles fall into two different groups (mean values 120.5(9) and 114.3(9)°) and there are three kinds of P-N-P angles (mean values 143.8(10), 136.6(11) and 131.2(11)°). The crystal structure shows some short intermolecular Br...Br distances (3.45, 3.45 and 3.48 Å).

The compound $N_5P_5F_{10}$ is a liquid at room temperature, the melting point is -50°C. In Chapter 3 a description is given of the apparatus and procedure used when growing single crystals of $N_5P_5F_{10}$ at low temperatures.

X-ray diffraction work revealed the existence of three different monoclinic modifications of $N_5P_5F_{10}$. We have determined the crystal and molecular structures of two of them, indicated by II and III. This work and the crystal structures are described in Chapter 4. The intensities of independent reflexions were measured at 110 K on a four-circle diffractometer with Mo radiation. The structures were solved by the symbolic addition method and refined by block-diagonal least-squares analysis. Modification II was refined with 1598 independent reflexions (θ = 0-25°) to R = 5.94 and R_w = 6.45%. For III two independent refinements were done using two different series of measured intensities. For

the first series (1096 reflexions; Θ = 0-25°) R and R_w are 6.77 and 6.76% respectively; the second series (1919 reflexions; Θ = 0-30°) gave R = 7.44 and R_w = 8.56%.

For modification II the mean P-N and P-F bond lengths are 1.549(5) and 1.528(3) Å. The mean N-P-N and F-P-F angles are 121.4(2) and 99.5(2)°. The P-N-P angles vary from 132.7 to 141.0(3)°. For III, corresponding bond lengths and valence angles obtained from the two refinements are the same within experimental error. The mean P-N and P-F bond lengths are 1.546(5) and 1.528(4) Å, the mean N-P-N and F-P-F angles are 120.9(3) and 99.3(3)°. The P-N-P angles vary from 133.9 till 151.6(4)°.

The conformation of the molecules is different in the two modifications. The molecules of II have a boat-shaped conformation. The shape of the molecules in III is rather irregular and ressembles that of the $N_5P_5Br_{10}$ molecules to some extent. Also the packing of the molecules in the crystals is different for the two modifications.

In Chapter 5 bond lengths, valence angles and molecular conformations of the compounds $N_nP_nX_{2n}$ with n = 3,4 and 5 and X = F,Cl and Br are discussed. For each molecule the P-N bond lengths are equal within experimental error. The small values (1.51 - 1.59 Å) observed for the P-N bond lengths in the compounds $N_nP_nX_{2n}$ may be explained by considering the combined effect of a σ and a π factor (see D.P.Craig and N.L. Paddock in "Nonbenzenoid Aromatics", II, Academic Press, New-York London, 1971). It was found that the π effect is constant in the group of molecules considered, and that the observed differences in P-N bond lengths are a consequence of the σ effect. No variation was thus found for the π effect as a function of the electronegativity of the substituent atoms, of the ring angles P-N-P and

N-P-N, or of the size of the ring.

On the other hand the endocyclic and exocyclic valence angles at phosphorus, N-P-N and X-P-X, were found to be dependent on the size of the ring. For n = 4 these angles are, on the average, some degrees larger than for n = 3 or 5. The same systematic behaviour is present in two other cyclophosphazene series. The relationship between the angles at phosphorus and the ring size could be explained by considering the relative importance of heteromorphic and homomorphic contributions to the π bonding in rings of different size.

The angles P-N-P were found to show a larger variation in their values than the angles N-P-N. For the eight-membered and ten-membered rings the P-N-P angles are expected to be somewhat larger than 150^{o} if the effect of P...P repulsion within a P-N-P group and the influence of σ and π bonding on the P-N-P angles is considered only. The values observed so far are generally smaller than 150^{o}, however. We have ascribed this reduction in value, which makes the molecules more compact, to the influence of intra- and intermolecular Van der Waals interaction. Evidently the gain in Van der Waals (attraction) energy obtained by making the molecules more compact balances the loss in σ and π bonding energy due to deviations of the P-N-P angles from their optimum values.

The molecular conformations of the pentameric halogenocyclophosphazenes show a strikingly large variation. This can be understood from the flexibility of the molecules (approximately free rotation around the P-N bonds) and from the fact that for these compounds the molecular conformations are influenced strongly by both intra- and intermolecular Van der Waals interactions.

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